The work to be presented in the thesis entitled "SYNTHESIS, CHARACTERIZATION, DYEING PERFORMANCE AND ANTIMICROBIAL STUDIES OF HETEROCYCLIC DISPERSE AND REACTIVE DYES" has been divided into five chapters.

CHAPTER 1: INTRODUCTION

Disperse dyes are organic colours with less water solubility, they are applied in colloidal aqueous dispersions to hydrophobic textile fibers in which dye literally dissolves to produce the desired colouration [1-3]. These are generally used to dye cellulose acetate, nylon, polyester and to some extent polypropylene, acrylic and modacrylic fibers. With increasing use of polyester fibers there has been found increased in development of disperse dyes. Azo dyes with a heterocyclic system are very useful class of disperse dyes [4-9]. The first member of disperse dye was introduced by British Dyestuff corporation namely–dispersol dyes in 1924, dispersed with soap or Turkey Red Oil (TRO). Simultaneously British cleanse company developed first disperse dye for the dyeing of secondary cellulose acetate [10]. They are known as SRA (Sulphated Ricinoleic Acid) [11]. The developments of such hydrophobic fibers created some problems in dyeing which resulted in the search of newer disperse dyes. Baddiley and Shoparadson solved the problem of dyeing acetate rayon with water insoluble dyestuff [12]. Development in azo disperse dyes over the last few decades has made it possible to produce a full range of bright shades with good fastness properties [13,14].

The first commercial synthetic dye, Mauveine, discovered by William Perkin in 1856 was also heterocyclic. Since that time the contribution of heterocyclic derivatives to colour chemistry has been considerable. Heterocyclic diazo and coupling components have played aristocratic role in azo disperse dyes chemistry. Some of the dyes based on heterocyclic ring system are known to possess high tinctorial power and excellent fastness properties towards certain substrate. Historically dyes derived from 2-amino thiazole, 2-amino benzothiazole and 2-amino-4-phenyl thiazole have played significant role in disperse dyes [15-18].

Thiazole [19-22] ring system is a stable ring system. The main approach of our work was to synthesize the disperse dyes consisting 2-amino-4-(3'-nitro phenyl) thiazole with azo substituent which has been further utilized to dye some hydrophobic fibers. The characteristic

data of different molecule were studied and further applied on polyester fibers to study their dyeing performance and fastness properties [23-26].

Reactive dyes are coloured compounds which contain one or two groups capable of forming covalent bonds between a carbon or dye atom of oxygen, nitrogen or sulphur atom of a hydroxyl, an amino or mercapto group, respectively of the substrate [27]. The most important distinguishing characteristic of reactive dyes is that they form covalent bonds with the substrate that is to be colored during the application process. Thus, the dye molecule contains specific functional groups that can undergo addition or substitution reactions with the OH, SH, and $NH_2$ groups present in textile fibers.

The first commercial reactive dye for cellulose was developed by Rattee and Stephen and marketed by ICI in 1956 under the trade name Procion M [28-31]. Several new reactive systems have been introduced from time to time, which covers the subject of innumerable patents and publication [32,33]. A large number of monochloro triazinyl reactive dyes have been synthesized for natural and synthetic fibers [34,35]. The presence of 1,3,5-triazine structure in the dye molecule improves their dyeing ability and possibility for application [36]. Hot brand reactive dyes have been widely considered due to their higher fixation yield on different fibers. Reactive dyes are becoming increasingly popular for dyeing cellulosic fibers because of their wide shade range, ease of application and excellent wet fastness properties. Improvement in the structure of reactive chromogens, selection and number of reactive groups led to an increased use of reactive dyes [37].

CHARACTERIZATION OF DYES

Infrared spectroscopy of selected synthetic dyes described in chapter 2 to 5 has been studied out for the structure elucidation of particular functional groups present in dye molecules. Nuclear Magnetic Resonance ($^1$H NMR) spectroscopy of some selected synthetic dyes described in chapter 2 to 5 has been studied for determination of structures of synthesized dyes using TMS as internal standard in DMSO solvent.

The synthesized compounds in chapter 2 to 5 were screened for their antimicrobial activity [38,39] by measuring zone of inhibition in mm. All the compounds were screened for their in vitro antimicrobial activity against different bacterial strains such as *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus, Bacillus subtilis* and fungi *Candida albicans*. Standard drugs like Ciprofloxacin and Flucanazole were used for the comparison purpose.

DYEING PERFORMANCE

Synthesized disperse dyes described in chapter 2 to 4 were applied on polyester fabrics. The reactive dyes described in chapter 5 were applied on cotton wool and silk fabrics, their fastness properties viz. light fastness, wash fastness, rubbing fastness, sublimation fastness have been evaluated. Visible spectra of the above dyes have been recorded to support the dyeing performance. Synthesized dyes were studied on colour matching computer for their dyeing performance as compared with reference.

Chapter 2 gives the synthesis of bisazo disperse dyes which were synthesized by using different amine and 3° amines. These different amines were diazotized and coupled with 2-amino -4-(3'-nitro phenyl) thiazole and then resulted compounds were further diazotized and coupled with different 3° amines in section 1, section 2 and section 3. These gave purple, pink, maroon, purple-brown, red, ruby red, brown and dark brown shades on polyester fabrics.

Synthesis of the dispersed dyes has been divided into three sections.

**Section 1.**

2-Amino-4-(3'-nitro phenyl)-5-(2",4"-dinitro phenyl) thiazole.

One mole of 2-amino-4-(3'-nitro phenyl)-5-(2",4"-dinitro phenyl) thiazole diazotized and was coupled with one mole of different 3° amines to yield different disperse dyes.

**Section 2.**

2-Amino-4-(3'-nitro phenyl)-5-(4"-fluoro phenyl) thiazole.

One mole of 2-amino-4-(3'-nitro phenyl)-5-(4"-fluoro phenyl) thiazole diazotized and was coupled with one mole of different 3° amines to yield different disperse dyes.

**Section 3.**

2-Amino-4-(3'-nitro phenyl)-5-(2",6"-dichloro,4"-nitro phenyl) thiazole.

One mole of 2-amino-4-(3'-nitro phenyl)-5-(2",6"-dichloro,4"-nitro phenyl) thiazole diazotized and was coupled with one mole of different 3° amines to yield different disperse dyes.

Chapter 3 describes the synthesis of disperse dyes which were synthesized by using different amines. These different amines were diazotized and coupled with couplers as described in section 1 and section 2. These gave yellow, orange, dark orange, red, cream, brown and dark brown shades on polyester fabrics.

Synthesis of the dispersed dyes has been divided into two sections.

**Section 1.**

N-(3-nitrophenyl)-2-((4-(3'-nitro phenyl)-1, 3-thiazol-2-yl) amino)acetamide.

One mole of different diazotized aryl amines was coupled with one mole of N-(3-nitrophenyl)-2-((4-(3'-nitro phenyl)-1,3-thiazol-2-yl) amino)acetamide to yield different disperse dyes.

**Section 2.**

N-(4-nitrophenyl)-2-((4-(3'-nitro phenyl)-1, 3-thiazol-2-yl) amino)acetamide.

One mole of different diazotized aryl amines was coupled with one mole of N-(4-nitrophenyl)-2-((4-(3'-nitro phenyl-1,3-thiazol-2-yl) amino)acetamide to yield different disperse dyes.

Chapter 4 provides the detail of work related to the synthesis of disperse dyes which were synthesized by using different amines. These different amines were diazotized and coupled with couplers as described in section 1 and section 2. These gave yellow, orange, red, cream, brown and dark brown shades on polyester fabrics.

Synthesis of the dispersed dyes has been divided into two sections.

**Section 1.**

N-(3-methylphenyl)-2-((4-(3'-nitro phenyl)-1, 3-thiazol-2-yl) amino)acetamide.

One mole of different diazotized aryl amines were coupled with one mole of N-(3-methyphenyl)-2-((4-(3'-nitro phenyl)-1, 3-thiazol-2-yl) amino)acetamide to yield different disperse dyes.

**Section 2.**

N-(4-methylphenyl)-2-((4-(3'-nitro phenyl)-1, 3-thiazol-2-yl) amino)acetamide.

One mole of different diazotized aryl amines were coupled with one mole of N-(4-methylphenyl)-2-((4-(3'-nitro phenyl)-1,3-thiazol-2-yl) amino)acetamide to yield different disperse dyes.

Chapter 5 gives the detail of the work related to the synthesis of reactive bifunctional reactive dyes which were synthesized by using different 2-amino substituted benzothiazole and amines. These different amines were diazotized and coupled with below mentioned couplers in section 1 and section 2. Their dyeing performance has been checked on cotton, wool, silk fabrics.

Synthesis of the reactive dyes has been divided into two sections.

**Section 1.**

2-((Substituted benzothiazol-2-yl)amino)-6-chloro-4-((4-(3'-nitrophenyl)thiazol-2-yl) amino)-1,3,5-triazine.

One mole of 2-((4-aminophenyl)sulfonyl)ethyl hydrogen sulfate diazotized and was coupled with one mole of 2-((substituted benzothiazol-2-yl)amino)-6-chloro-4-((4-(3'-nitrophenyl)thiazol-2-yl)amino)-1,3,5-triazine to yield different reactive dyes.

**Section 2.**

2-((4-((4-Chloro-6-((4-(3'-nitrophenyl) thiazol-2-yl)amino)-1,3,5-triazin-2-yl)amino)phenyl) sulfonyl)ethyl hydrogen sulfate.

One mole of different diazotized aryl amines was coupled with one mole of 2-((4-((4-chloro-6-((4-(3'-nitrophenyl)thiazol-2-yl)amino)-1,3,5-triazin-2-yl)amino)phenyl)sulfonyl)ethyl hydrogen sulfate to yield different reactive dyes.

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